

US EPA ARCHIVE DOCUMENT

# **Atmospheric Processing of Organic Particulate Matter: Formation, Properties, Long-Range Transport, and Removal**

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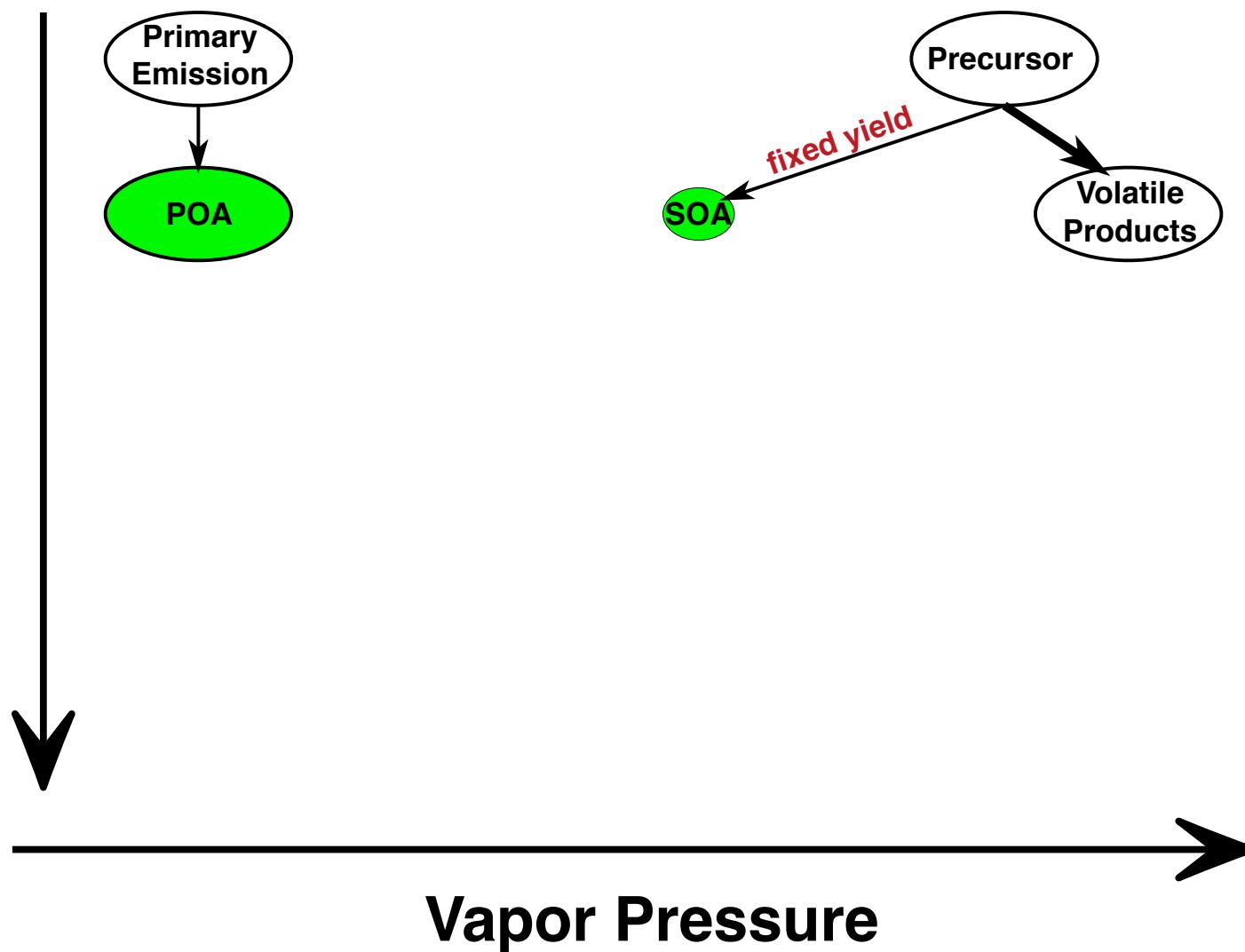
Carnegie Mellon University  
Center for Atmospheric Particle Studies

Atmospheric Science Progress Review Meeting  
22 Jun 2007  
RTP, NC

# The Center for Atmospheric Particle Studies

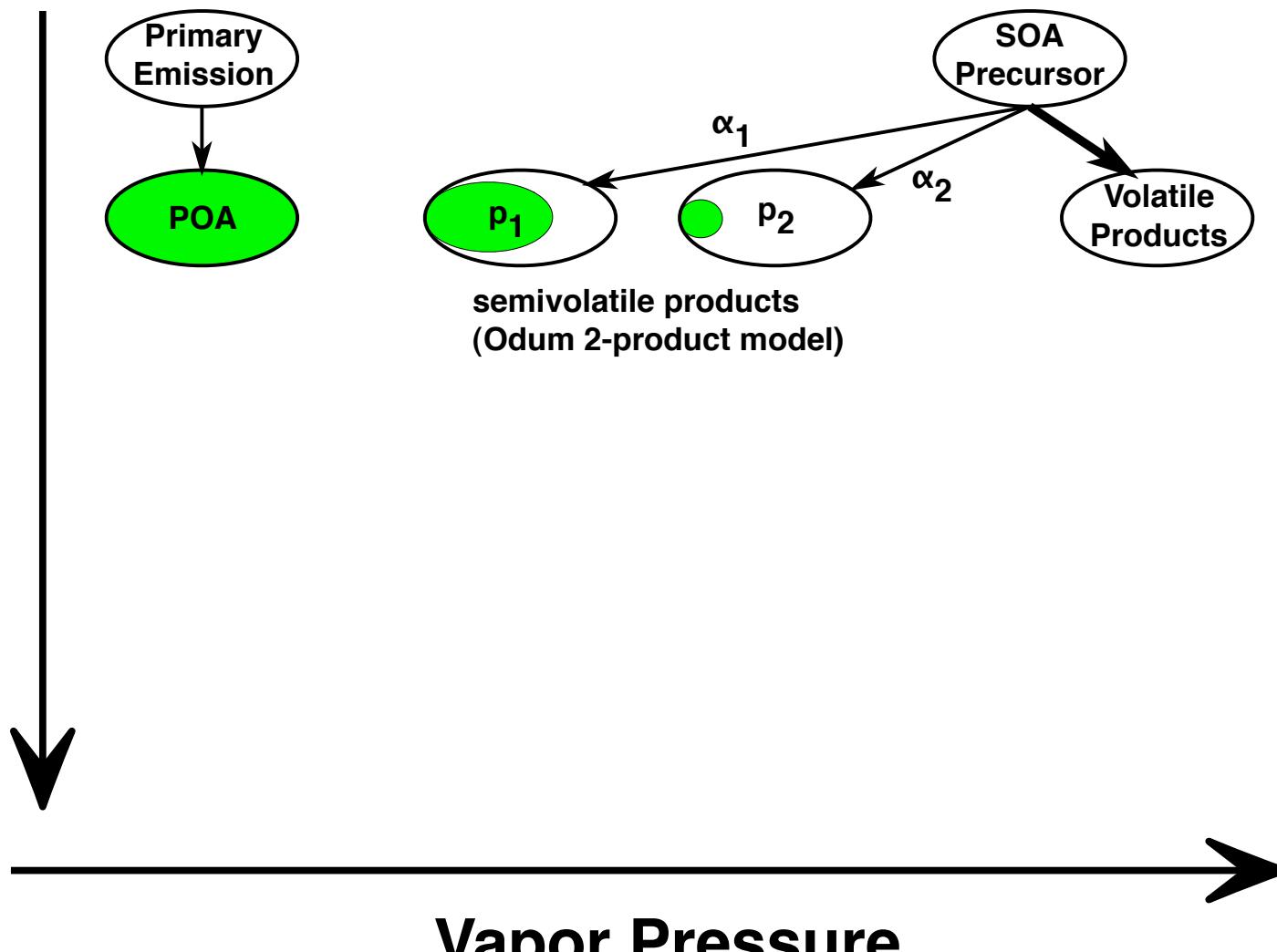


# Organic Aerosol



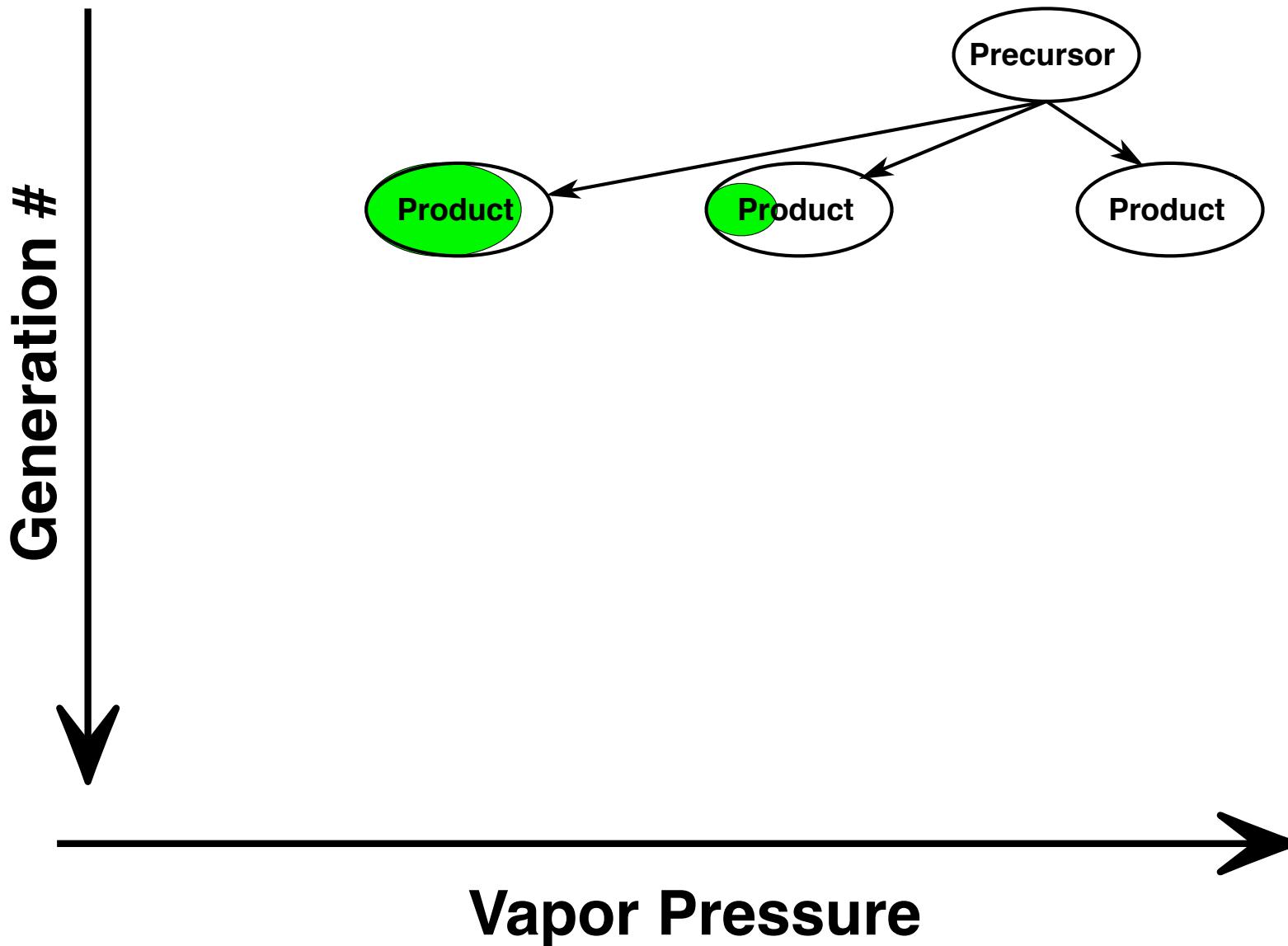
*Not quite state of the art, common in models...*

# Organic Aerosol

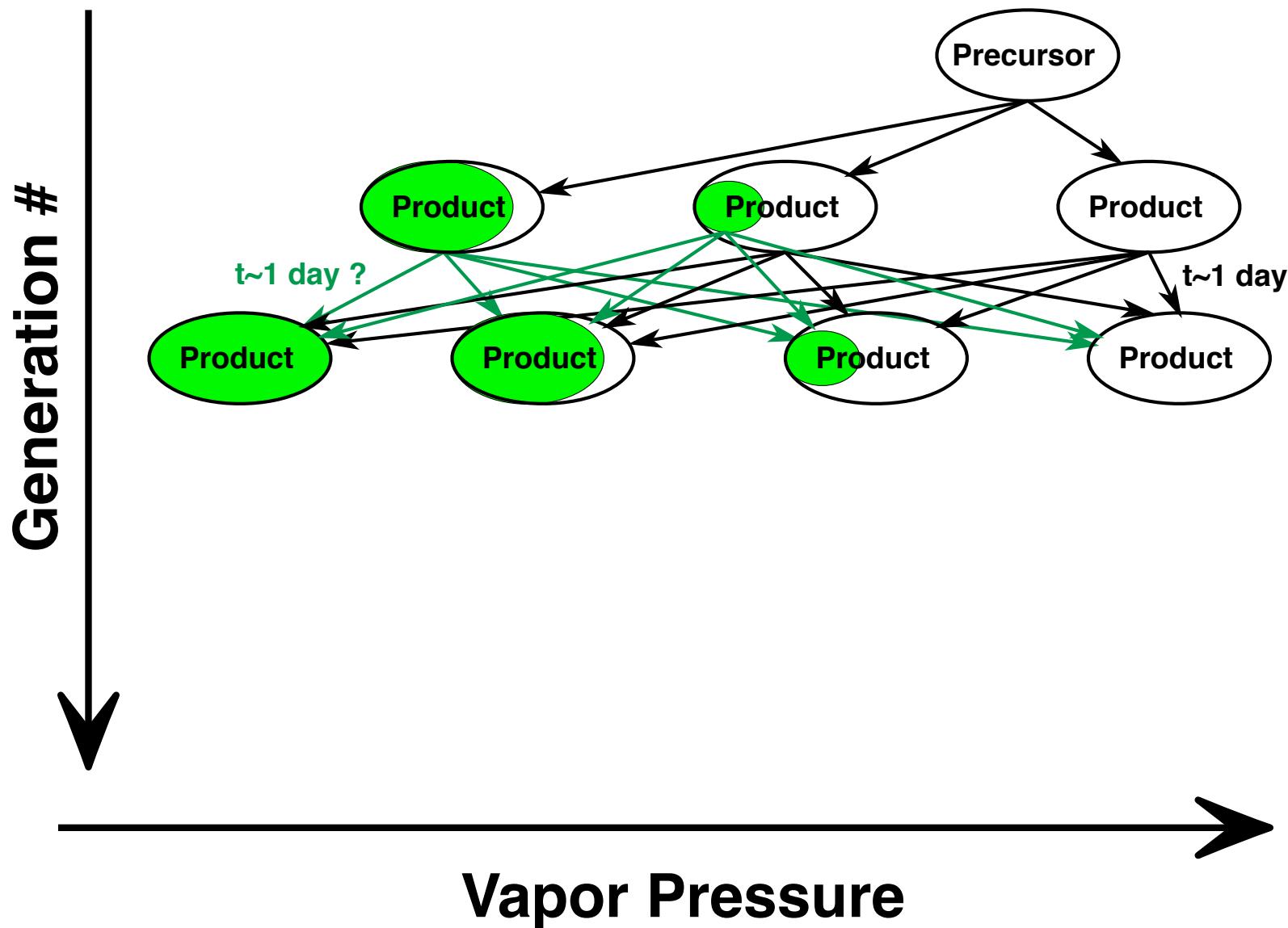


*State of the art, in some models...*

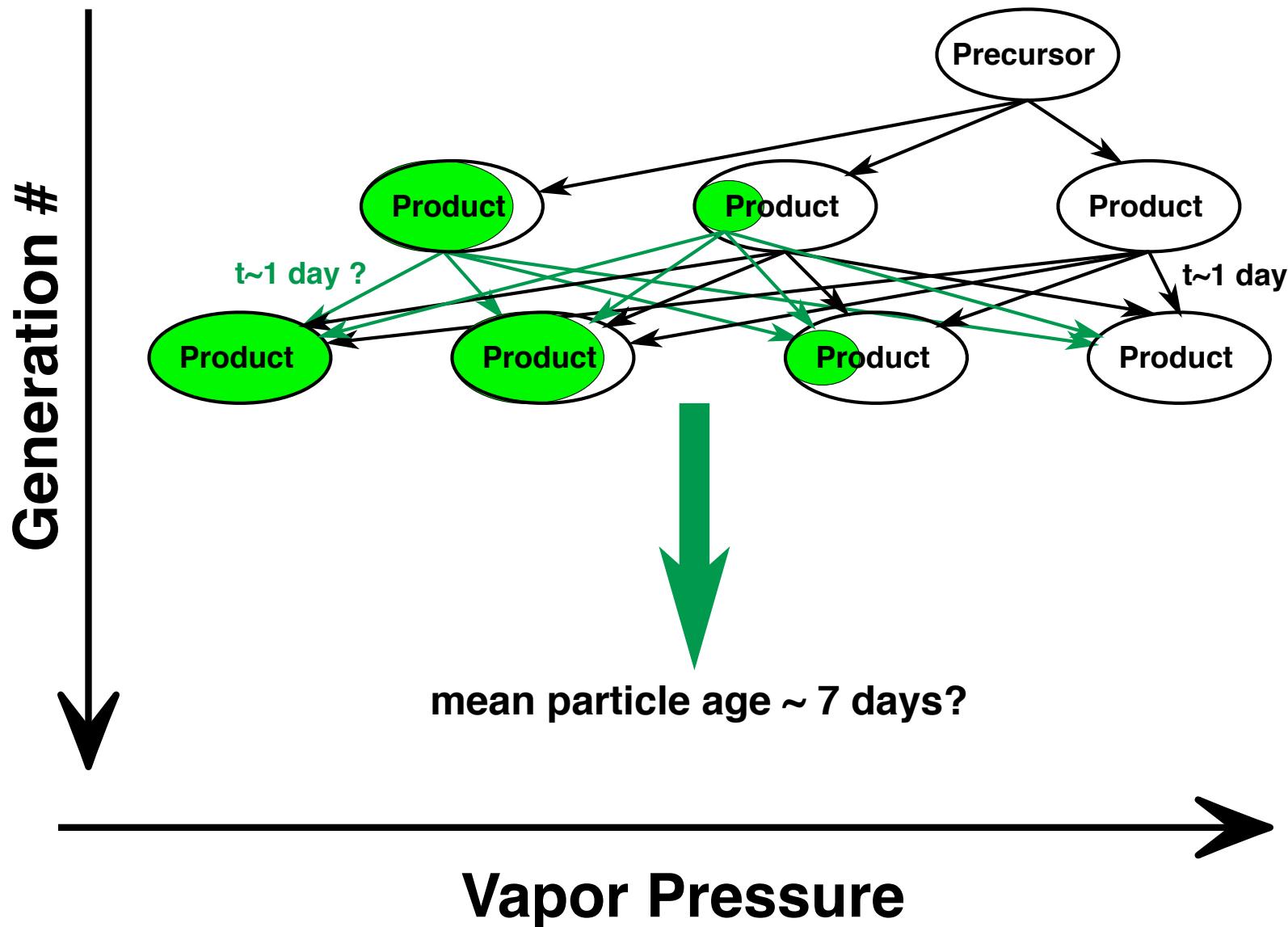
# Organic Emissions Processing



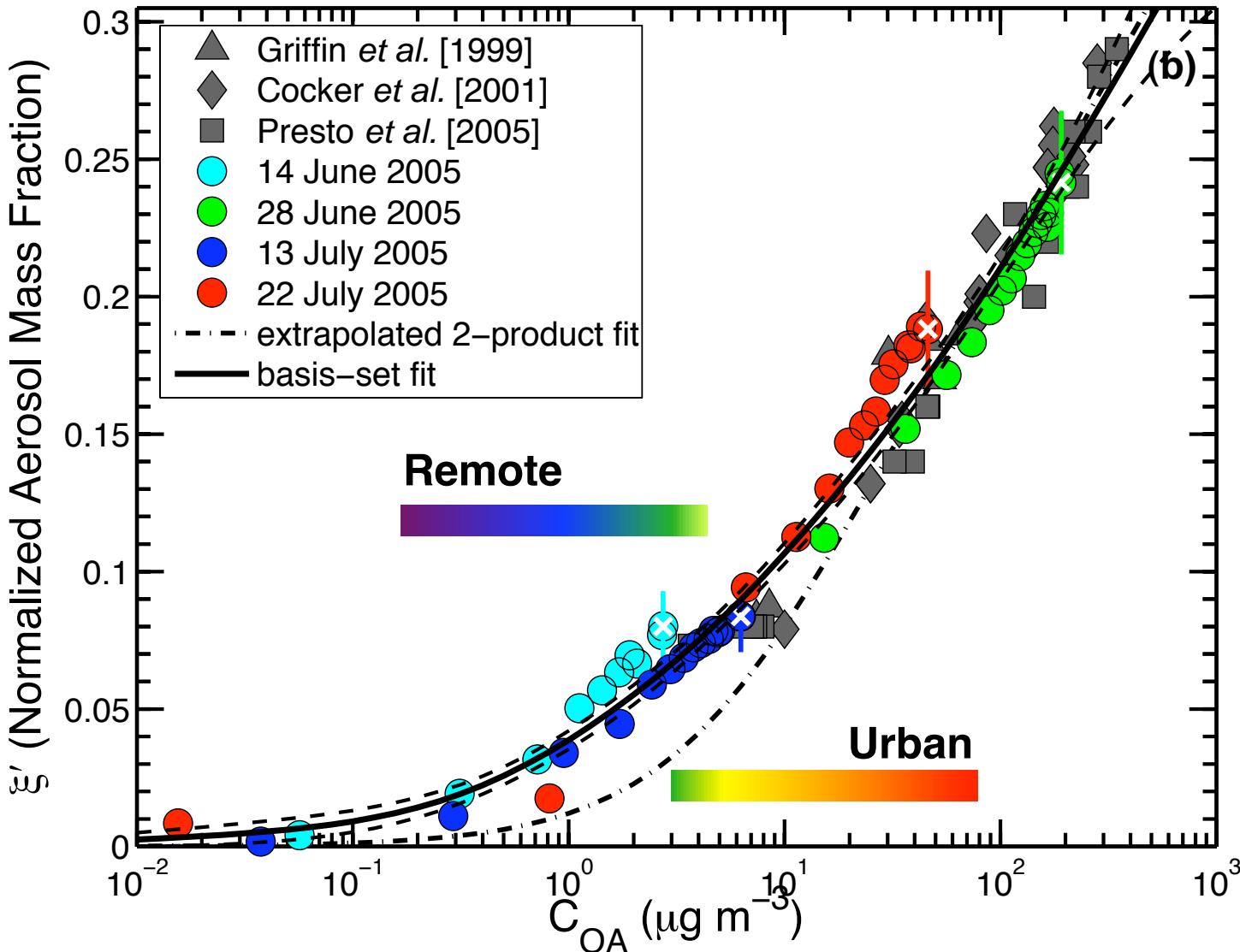
# Continued Processing



# How Far Does it Go??



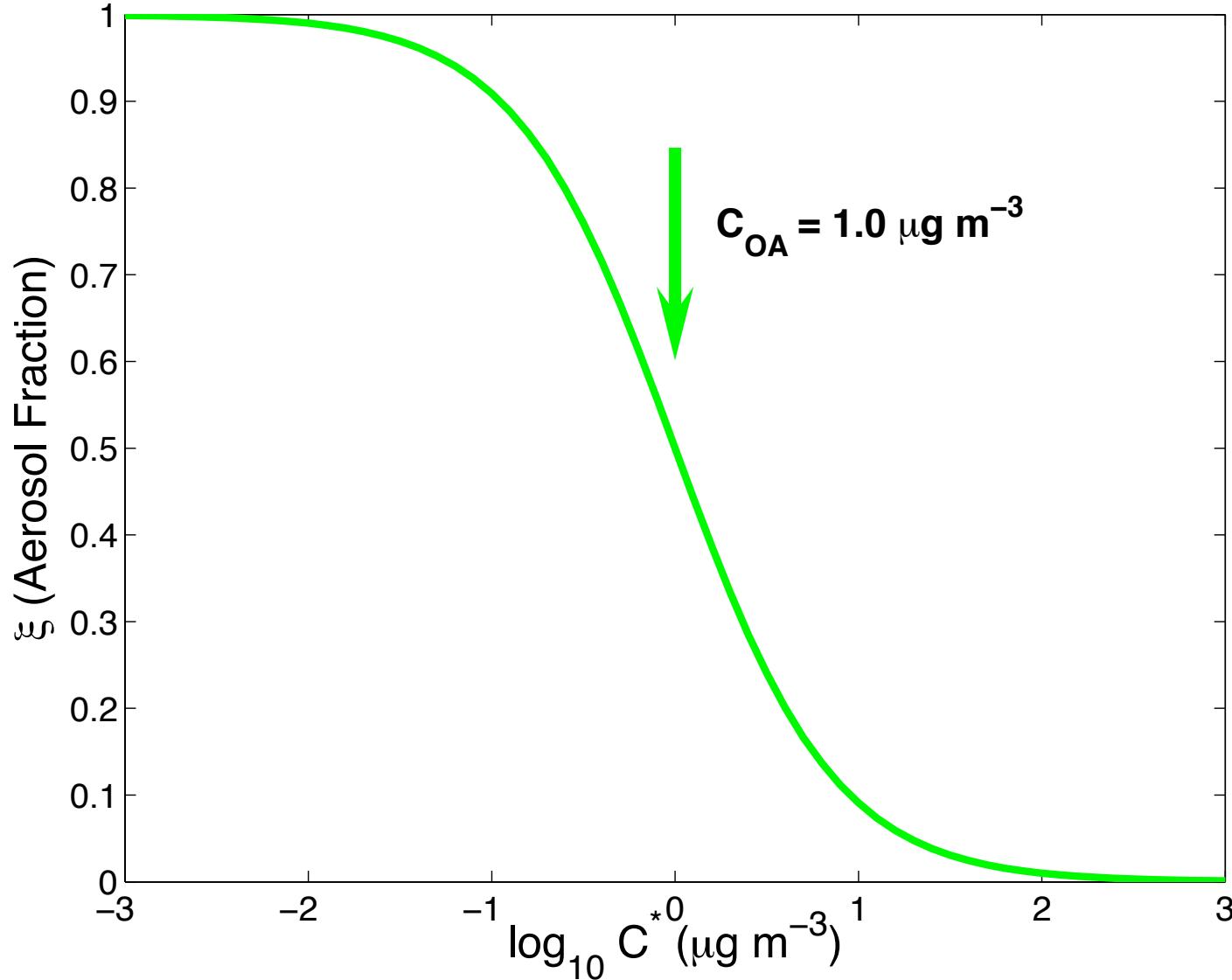
# $\alpha$ -pinene + Ozone



~ 2x SOA under remote atmospheric conditions vs. extrapolation.

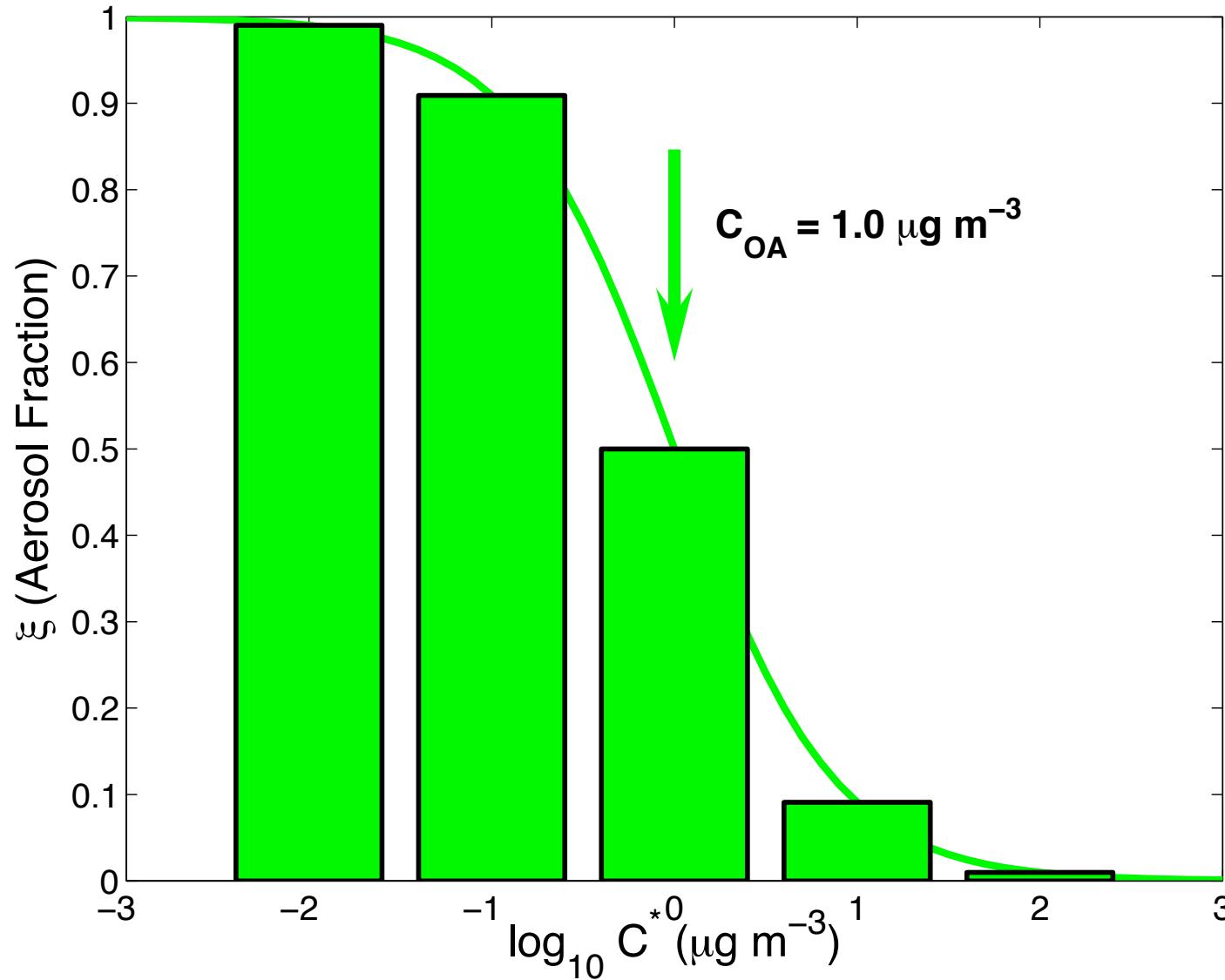
[Presto and Donahue, *ES&T*, 2006]

# Partitioning at Specified $C_{OA}$ in Solution



$$\xi_i = \frac{1}{1 + \frac{C_i^*}{C_{OA}}}$$

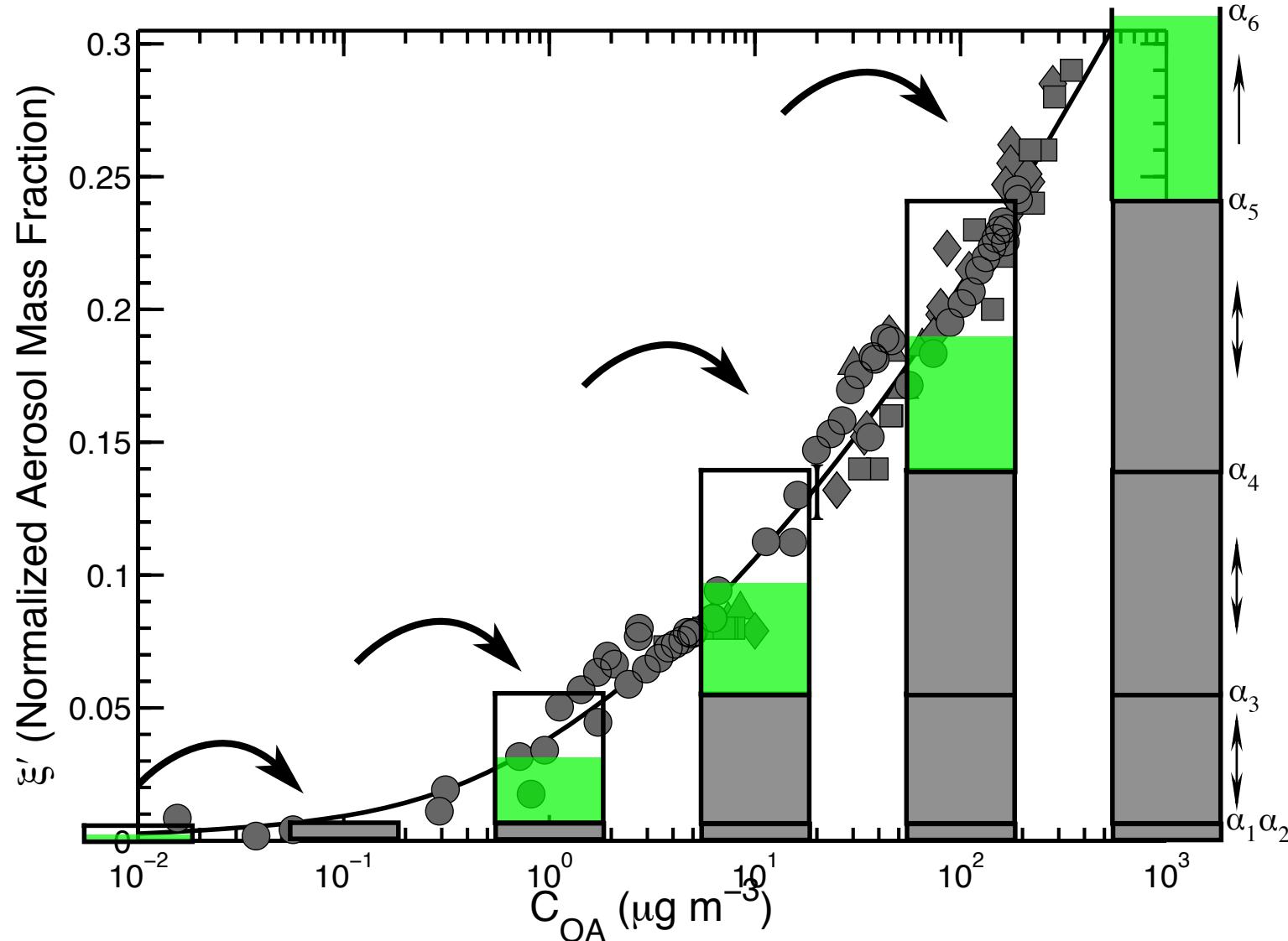
# The Volatility Basis Set



$$C_i^* = \{0.01, 0.1, 1, 10, 100, 1000, 10^4, 10^5, 10^6\} \mu\text{g m}^{-3}$$

[Donahue *et al.*, *ES&T*, 2006]

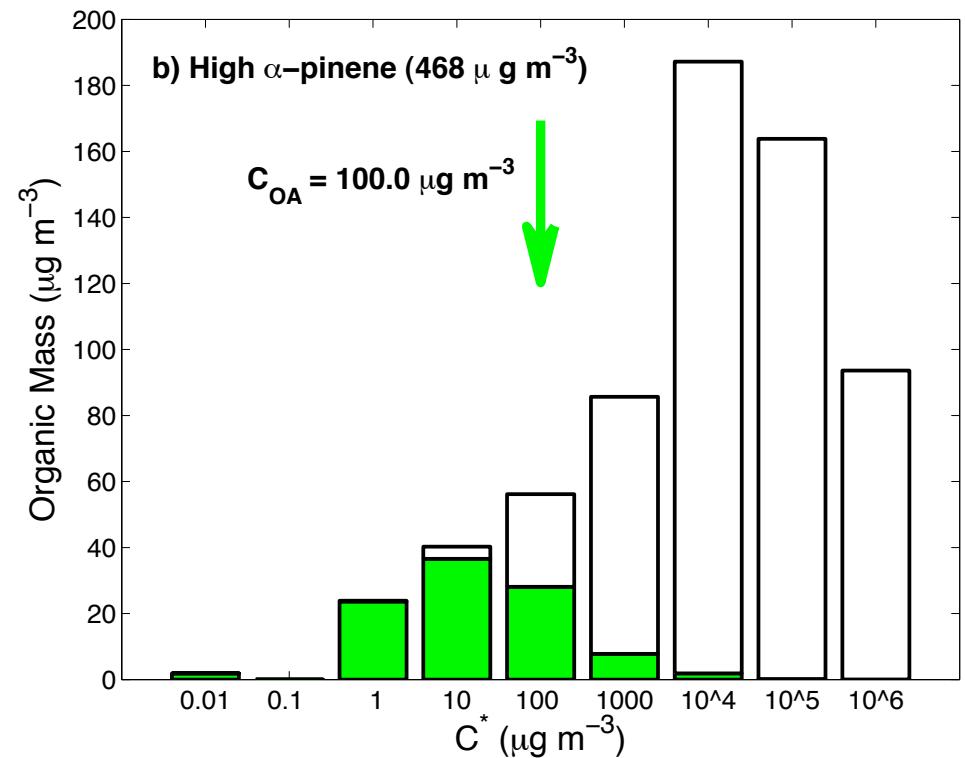
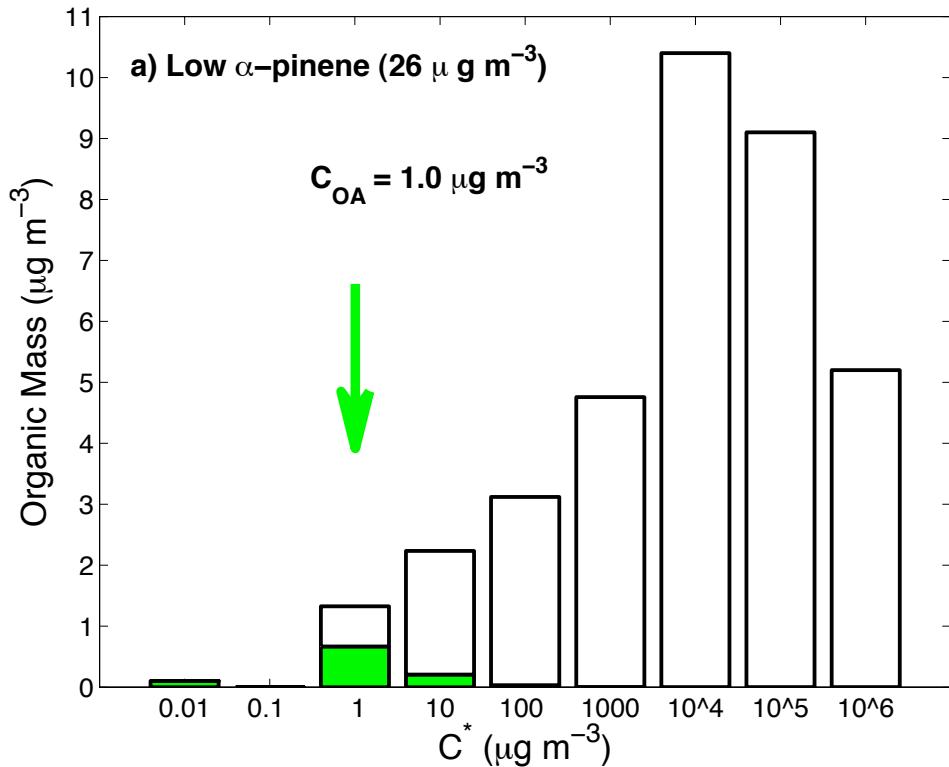
# $\alpha$ -pinene and the Basis Set



(mass yields  $\alpha'$ )

$$\alpha'_i = \{ .004, 0, .05, .09, .12, .18, \dots \}$$

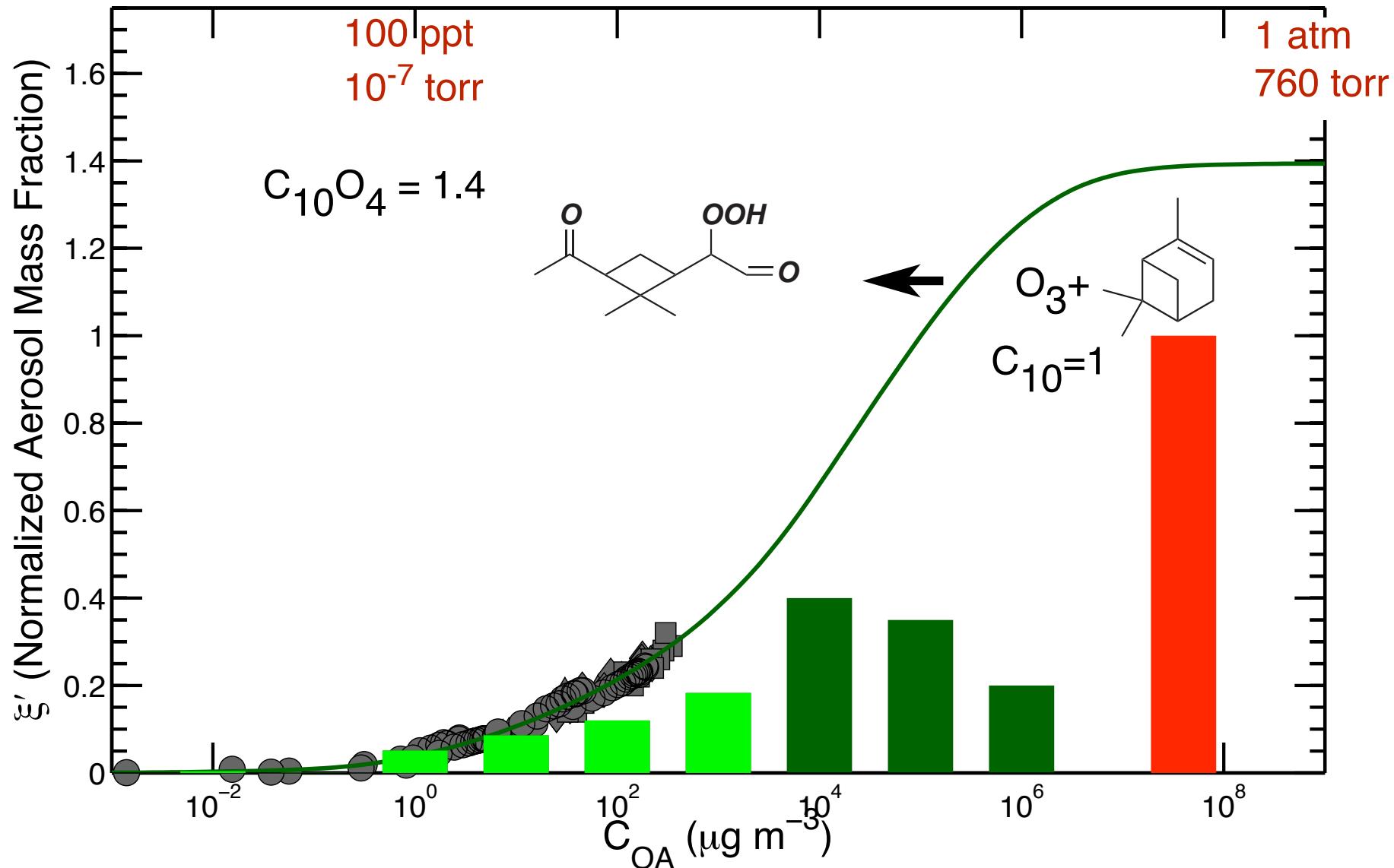
# $\alpha$ -Pinene + Ozone Partitioning



Partitioning changes with mass loading:  $\times 18$  total loading =  $\times 100 C_{\text{OA}}$ .  
Most of the OA compounds at  $100 \mu\text{g m}^{-3}$  are not in the particles at 1.

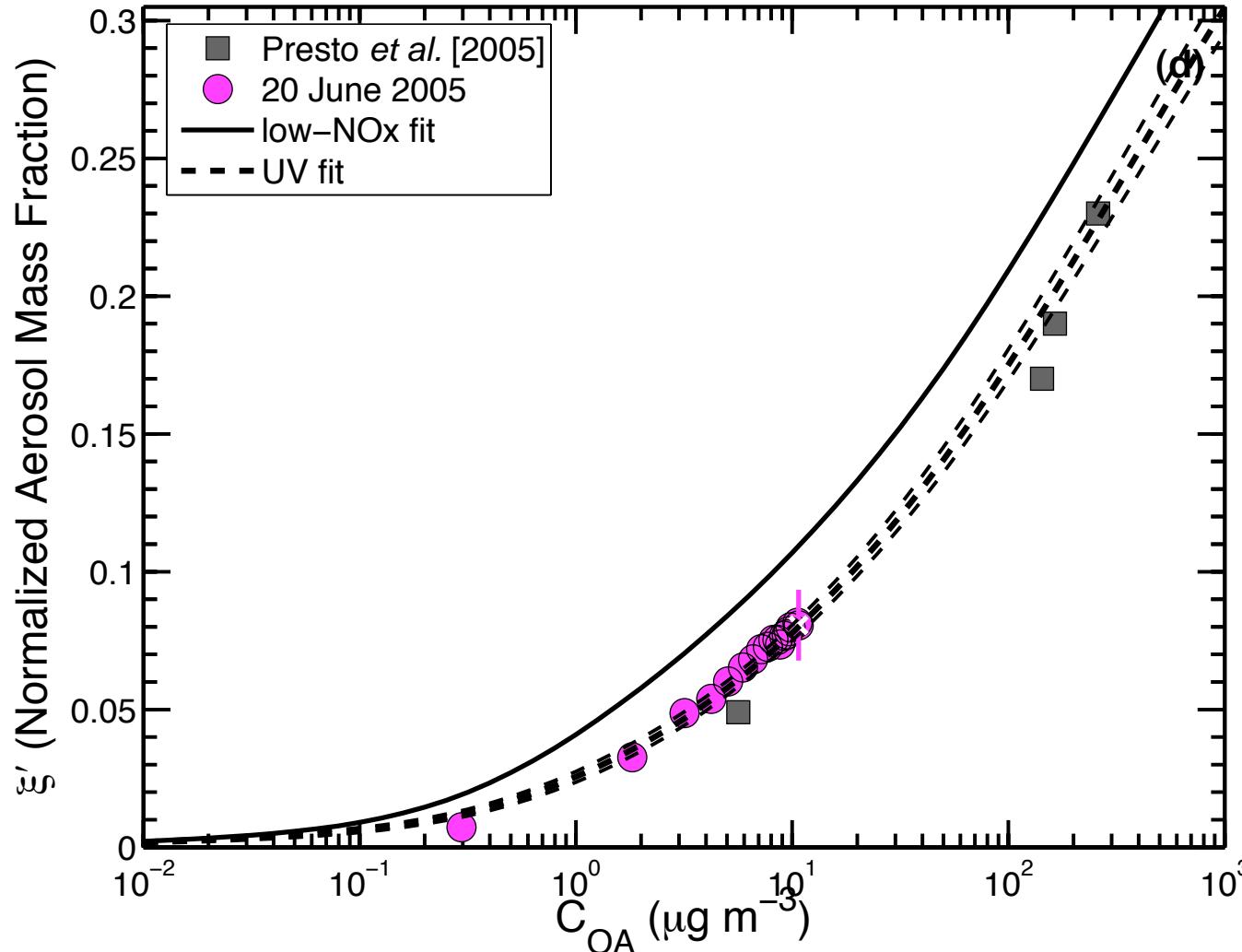
[Donahue *et al.* in prep]

# $\alpha$ -Pinene + Ozone Mass Balance



Mass balance for 'nominal product' demands  $\xi_{\max} = \sum_i \alpha_i \simeq 1.4$ .

# $\alpha$ -pinene + Ozone: UV (no NO<sub>x</sub>)



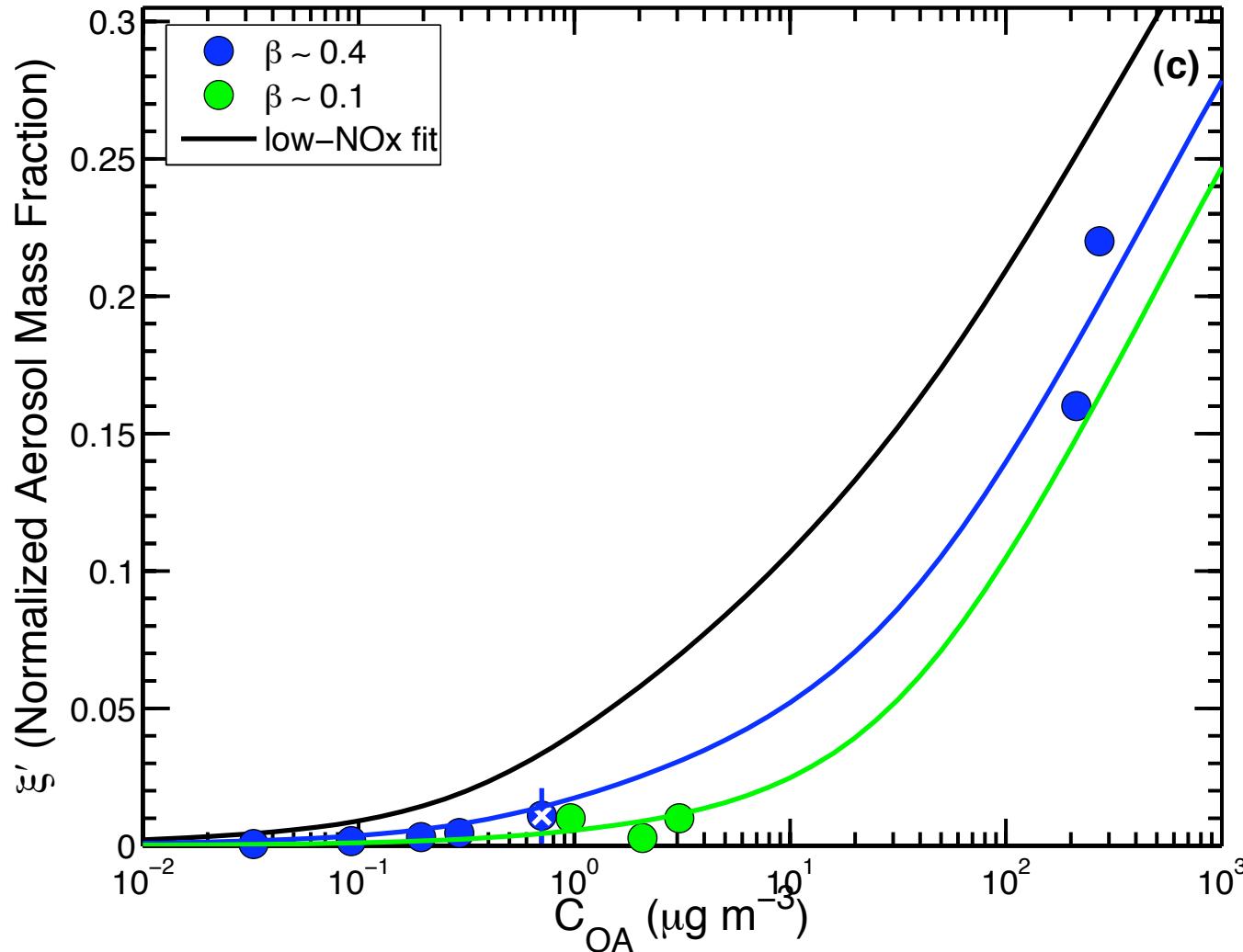
$$\alpha'_i = \{ .004, 0, .05, .09, .12, .18, \dots \}$$

↓ UV

$$\alpha'_i(\text{UV}) = \{ .004, 0, .02, .08, .12, .18, \dots \}$$

[Presto *et al.*, *ES&T*, 2005a]

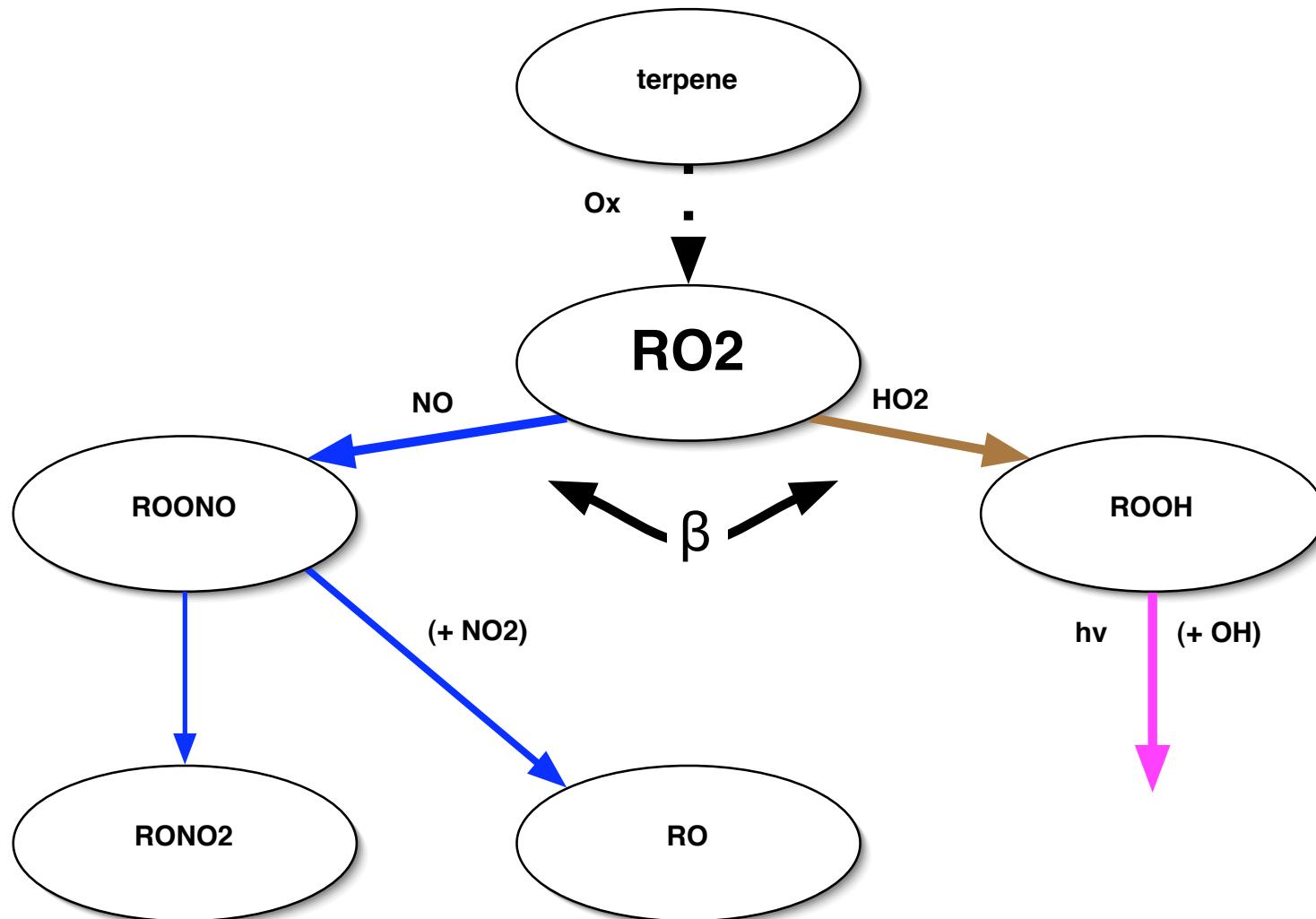
# $\alpha$ -pinene + Ozone: VOC:NO<sub>x</sub>



$$\begin{aligned}\alpha'_i(\text{HO}_2) &= \{.004, 0, .05, .09, .12, .18, \dots\} \\ \downarrow \text{NO}_x \quad \beta &= (\text{VOC : NO}_x)_0 / 10, (\text{VOC : NO}_x)_0 < 10 \\ \alpha'_i(\text{NO}_x) &= \{0, 0, 0, 0, .15, .2, \dots\}\end{aligned}$$

[Presto *et al.*, *ES&T*, 2005b]

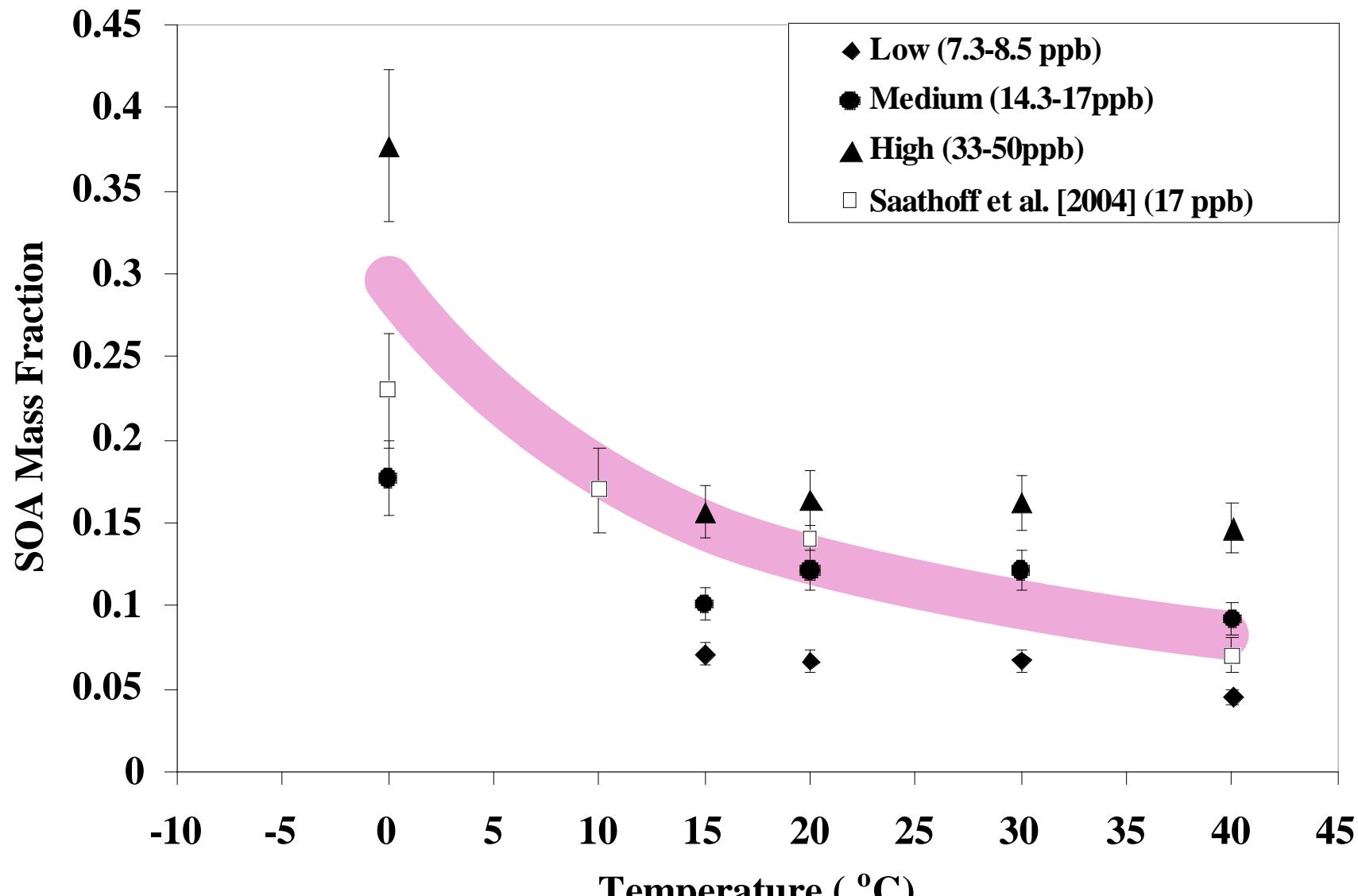
# RO<sub>2</sub> Fate



Bottom line – tie SOA module into gas-phase RO<sub>2</sub> chemistry:

$$\{\alpha\} = \beta \{\alpha\}^{\text{low-NO}_x} + (1 - \beta) \{\alpha\}^{\text{high-NO}_x}$$

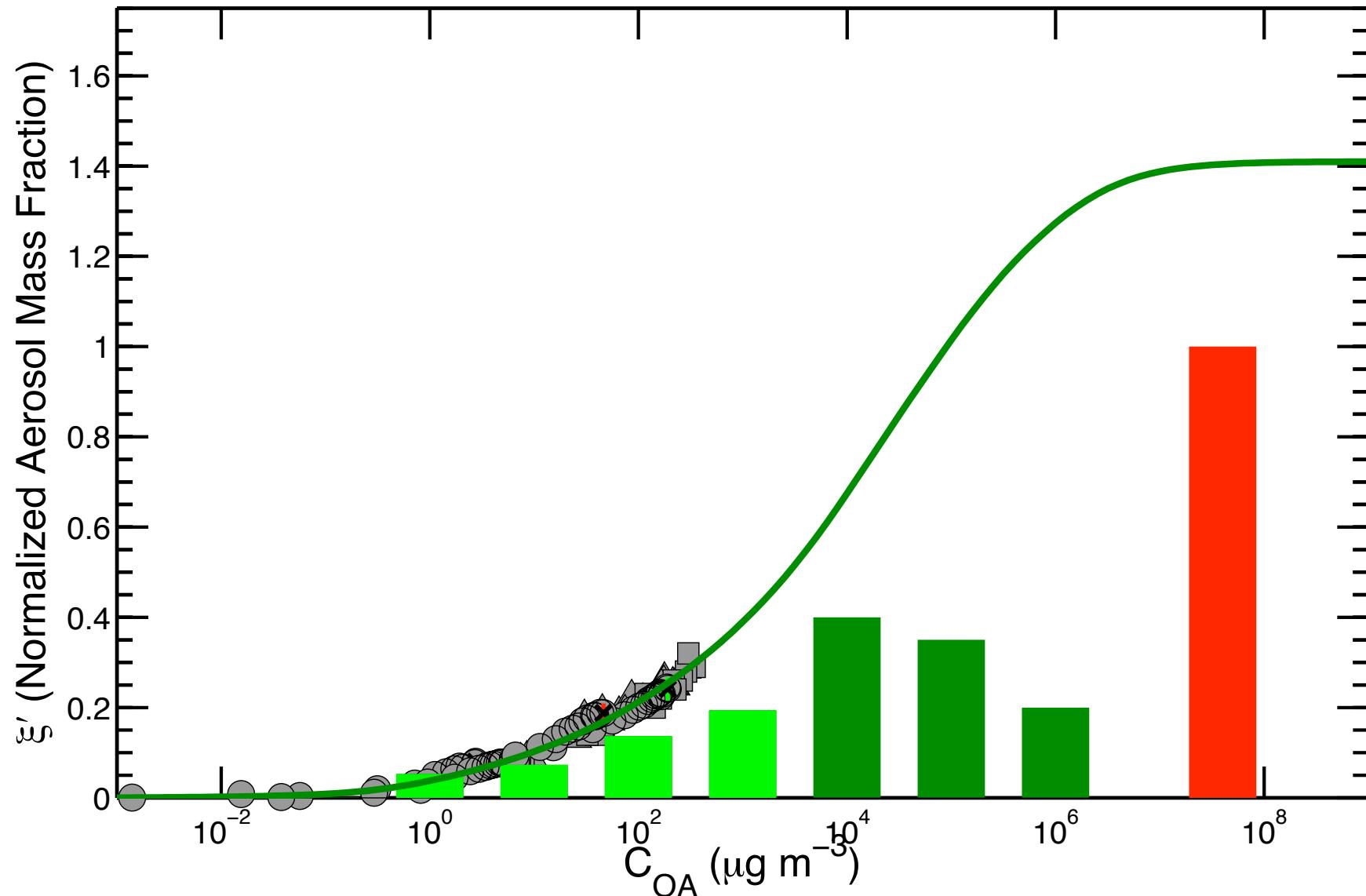
# $\alpha$ -Pinene + Ozone T Dependence



Upturn in SOA between 15 and 0°C.

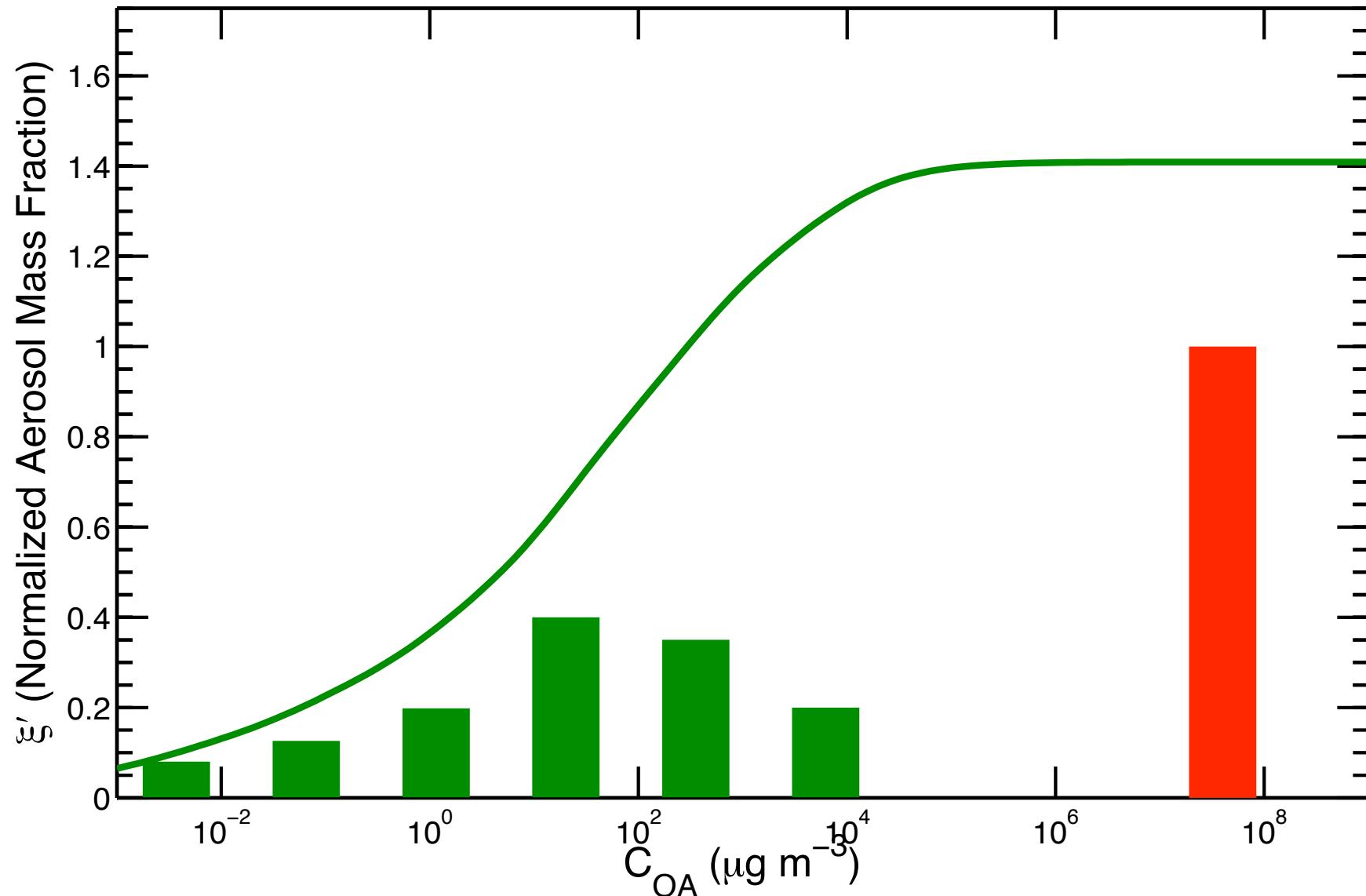
[Pathak *et al.*, *JGR*, 2007], [Stanier *et al.*, *ACPD*, 2007]

# $\alpha$ -Pinene + Ozone Total Mass 300 K



Dark green yields are guesses – total is constrained.

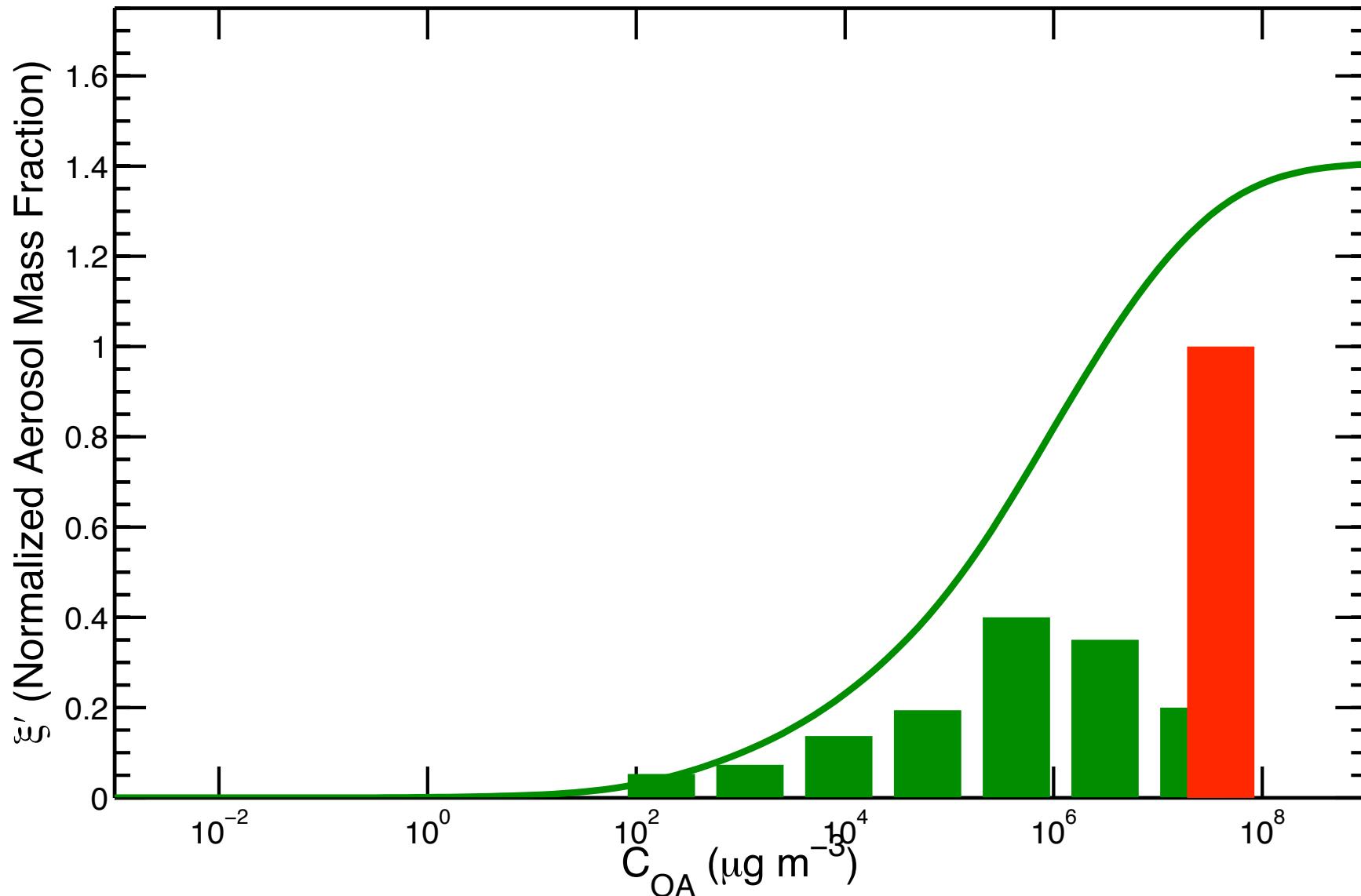
# $\alpha$ -Pinene + Ozone Total Mass 243 K



Products shift left by 2.5 orders of magnitude.

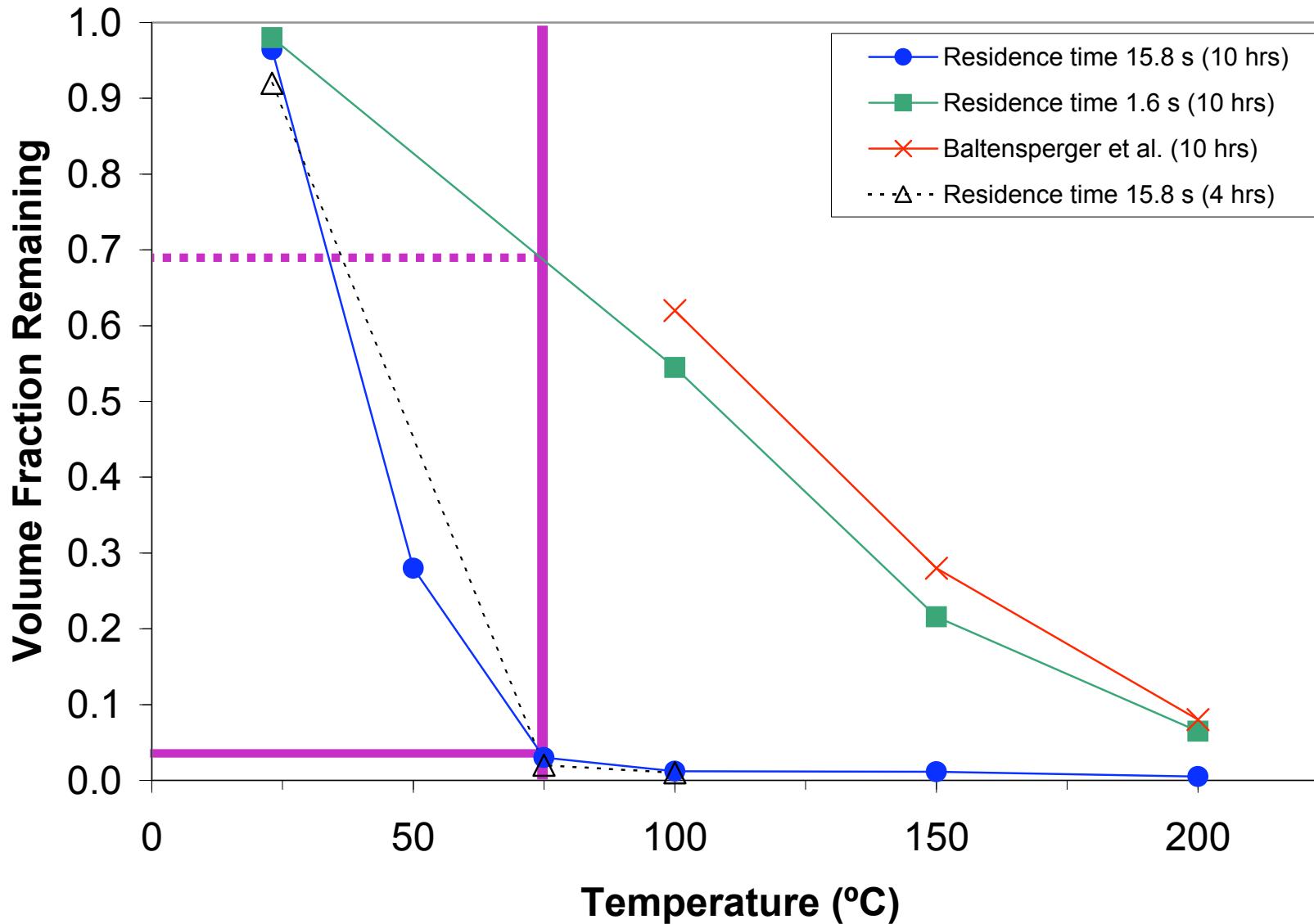
(Note – [Saathoff *et al.* IAC 2006] saw  $\sim 1$  AMF at 100-200  $\mu\text{g m}^{-3}$  and 243 K.)

# $\alpha$ -Pinene + Ozone Total Mass 350 K



Products shift right by 2.5 orders of magnitude.

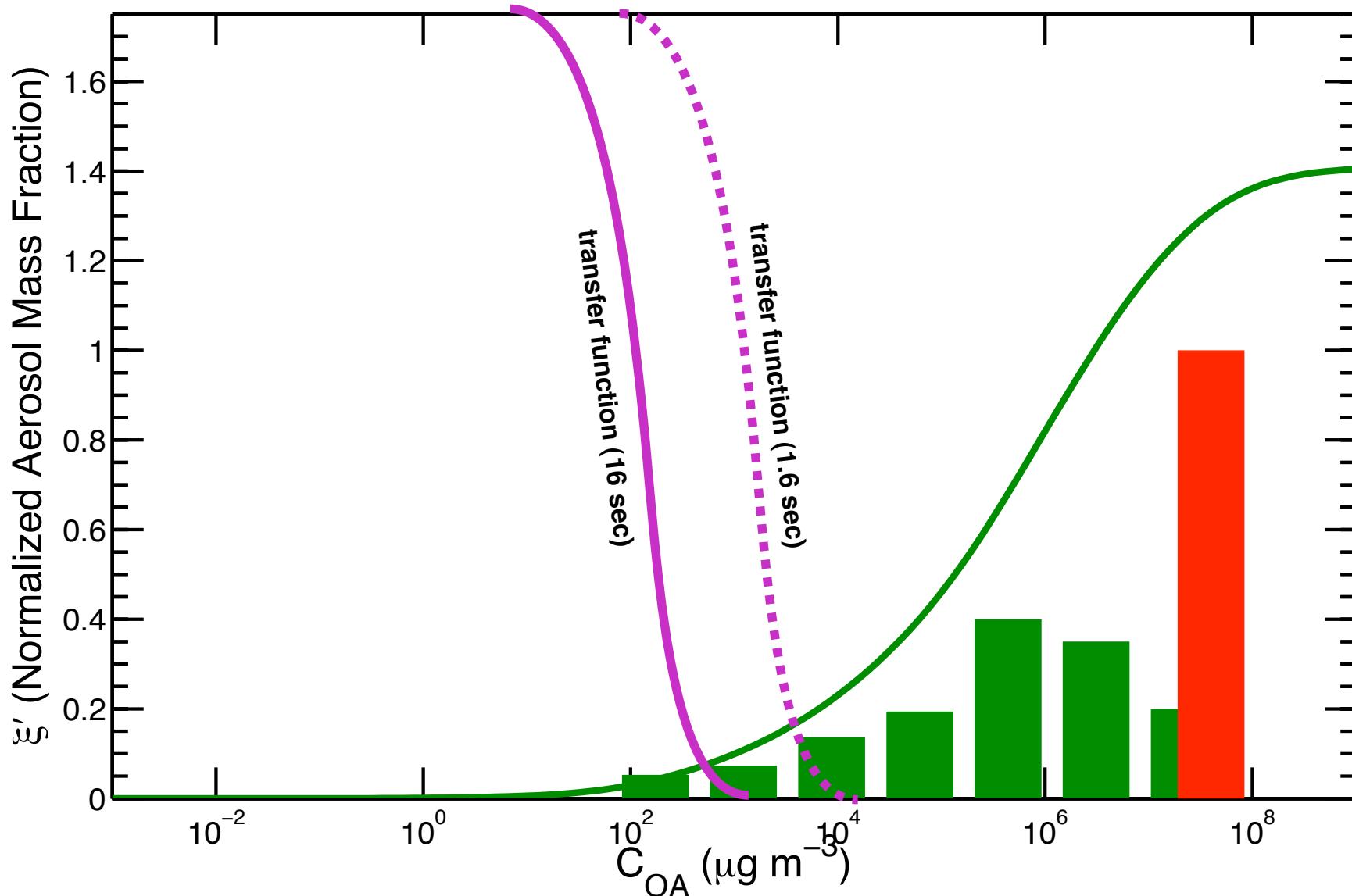
# $\alpha$ -Pinene + Ozone Thermodenuder



Given time, *all* SOA evaporates at 70C.

[An *et al.*, AS&T, 2007]

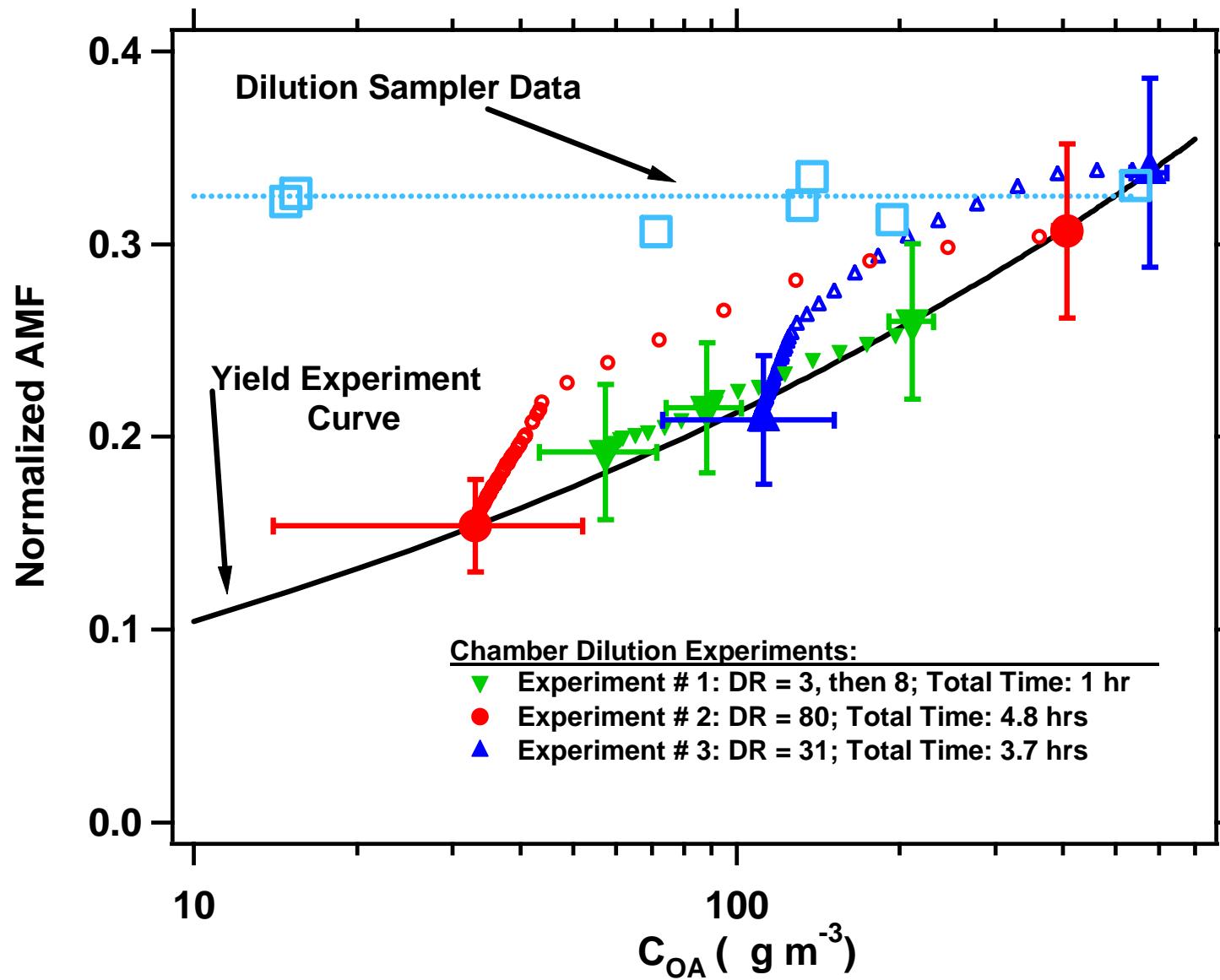
# $\alpha$ -Pinene + Ozone Thermodenuder



Denuding is a function of evaporation timescales.

[Pierce *et al.*, *in prep*, 2007]

# $\alpha$ -pinene + O<sub>3</sub> Dilution

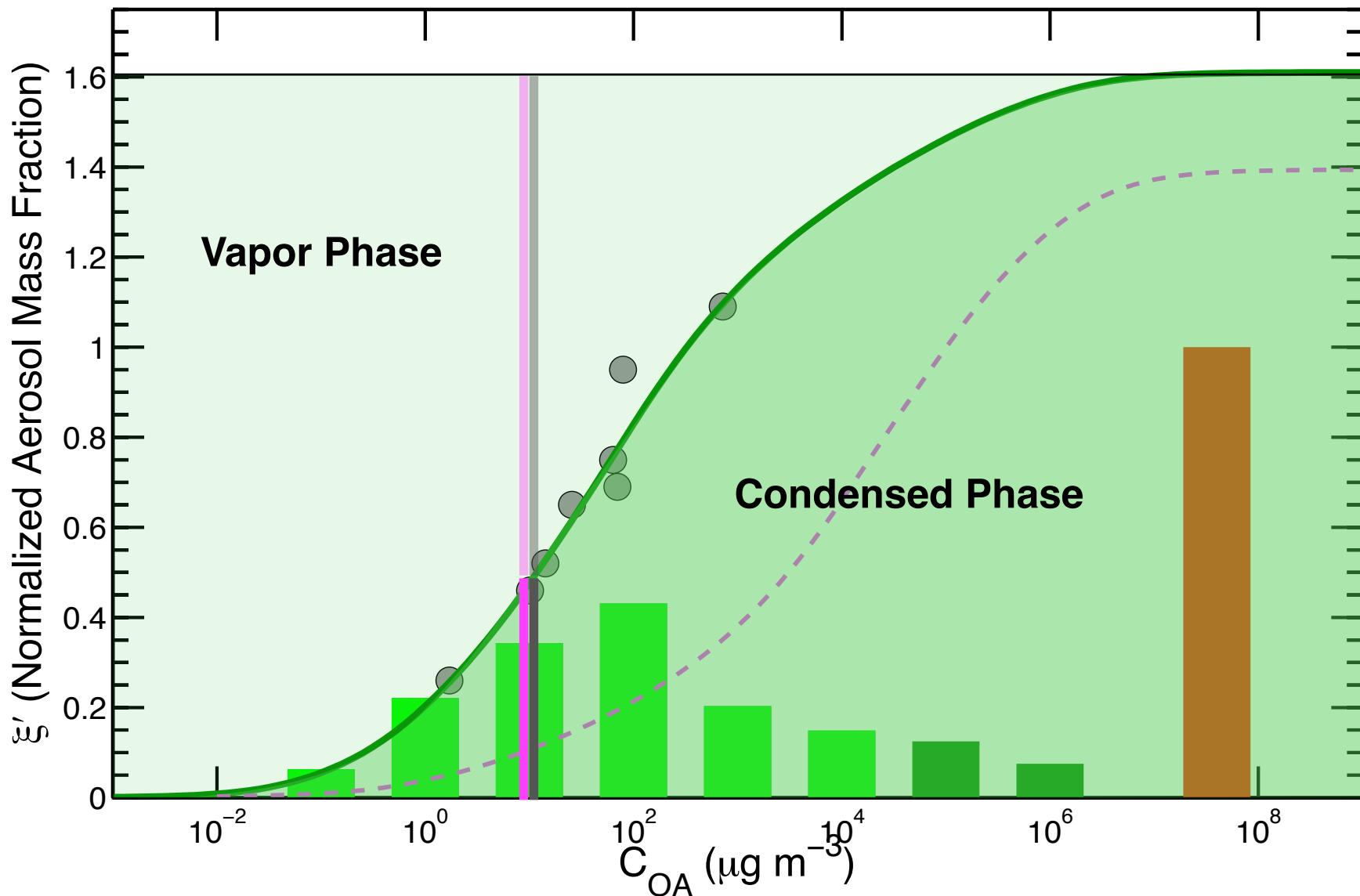


Generate high SOA and then flush 90% of chamber air.

Particles shrink *slowly* to expected size.

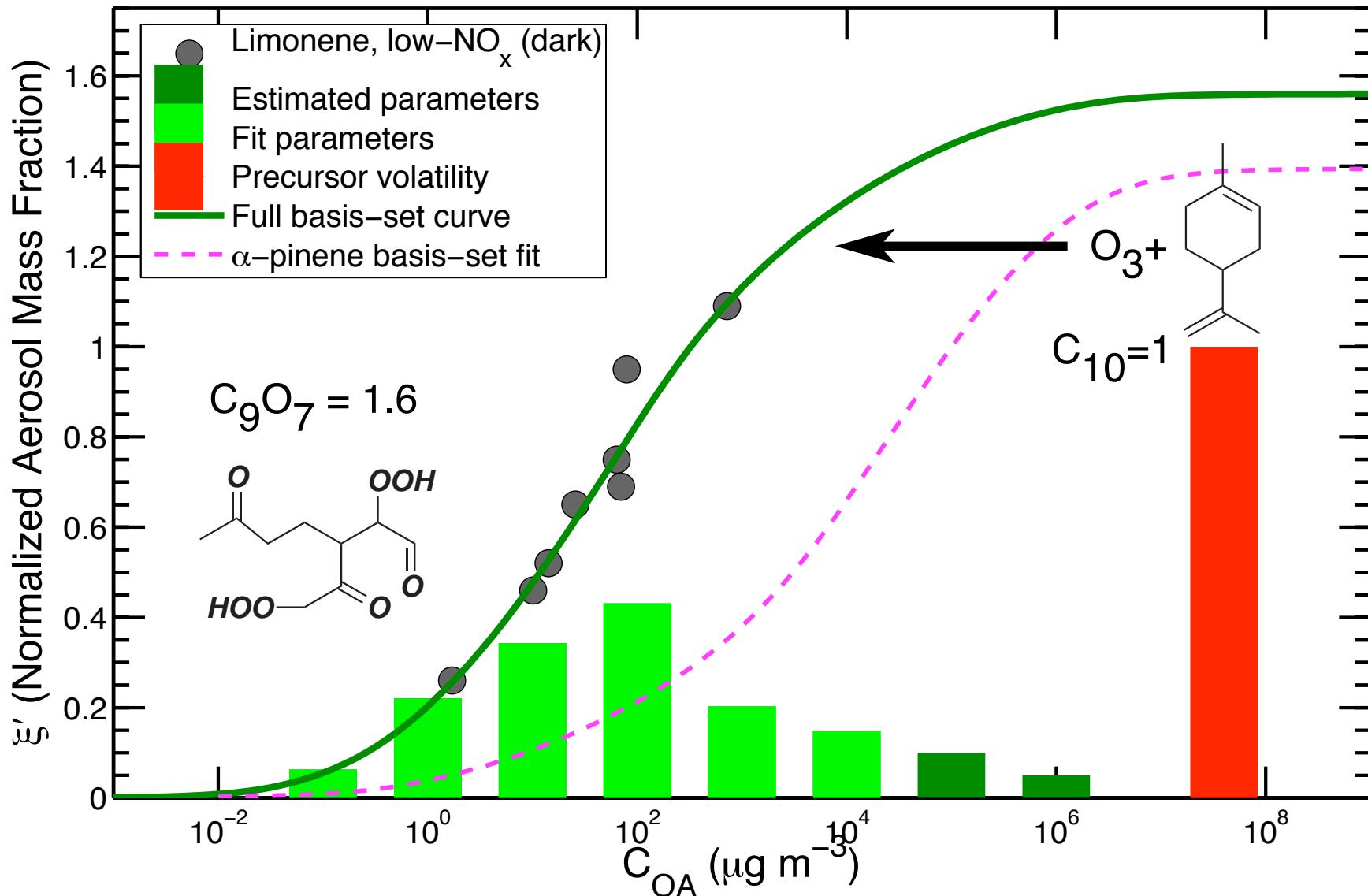
[Grieshop *et al.*, GRL 2007]

# Implications: Vapors



The mass not seen in the particles is in the gas phase, very low vapor pressure.

# Limonene + Ozone Mass Balance

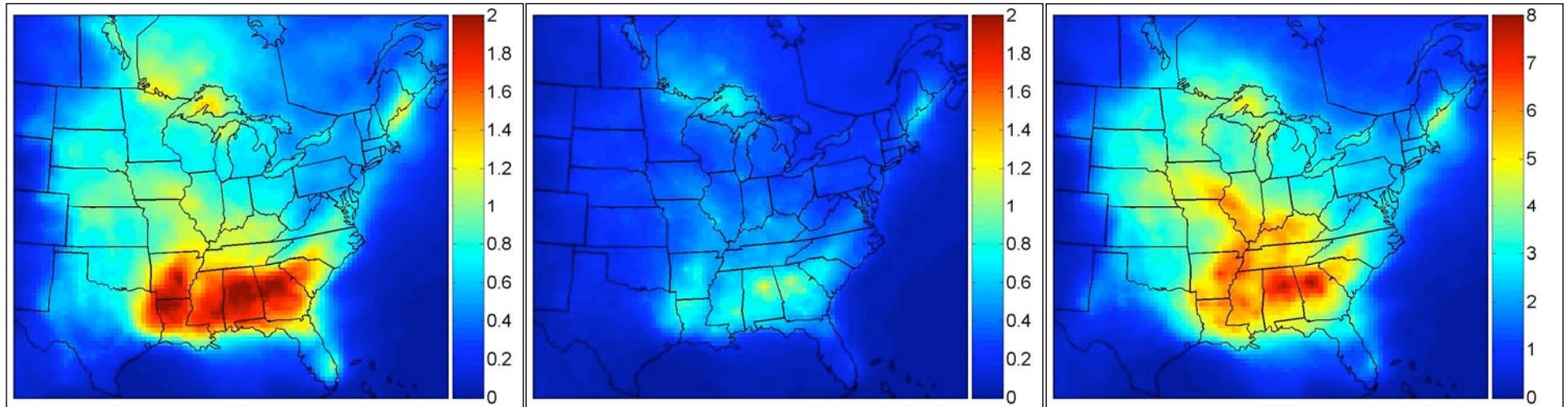


D-limonene +  $\text{O}_3$  makes more SOA than  $\alpha$ -pinene (2nd generation of oxidation).

[J. Zhang *et al.*, JPC, 2006]

# Implementing Basis Set in PMCAMx

July 2001 Biogenic SOA



Old ~constant yield

New Basis set yields

Multi-generation aging

New basis set parameters cause most SOA to evaporate at ambient  $C_{OA}$ .  
Adding aging (gas-phase OH oxidation) can generate *lots* of SOA.  
Aging parameters are not yet known (these are a reasonable guess).

[Lane *et al.* in prep]

# Conclusions Picture

